8-1972

A Study of the Blocking of Polyvinylidene Chloride in a Rewound Roll

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A STUDY OF THE BLOCKING OF POLYVINYLIDENE CHLORIDE IN A REWOUND ROLL

by

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A Thesis submitted to the
Faculty of the Department of Paper Technology
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan
August 1972

ABSTRACT

The blocking tendency of polyvinylidene chloride (PVDC) coated paper, front to back, in a rewound roll against a clay-coated surface was investigated. Pressure, temperature, contact time, relative humidity, and thickness of the PVDC layer or layers were all found to be important in the blocking of PVDC coated paper. Autohesion was considered to be the most probable mechanism of blocking. Autohesion involves the interweaving of the polymer molecules of both coated surfaces when they are in contact and under pressure at high temperatures. One way of eliminating blocking is by completely drying (crystallizing) the PVDC film and thereby reducing the effect of contact time and pressure. Another way of eliminating blocking, the one investigated in this paper, is by using an anti-blocking agent in the clay-coating. Anti-blocking agents influence the flow characteristics of the coating and thereby affect adhesive migration. It is this influence that is attributed with reducing the affinity of the polymeric adhesive, in the clay-coating, for the PVDC film and thus preventing blocking. One paraffin wax emulsion, particularly, when used in large amounts and with large amounts of starch prevented blocking.

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INTRODUCTION

Polyvinylidene chloride copolymers, known as PVDC, exhibit outstanding barrier and heat sealability properties as surface coatings for packaging materials. These polymers are odorless, tasteless, nontoxic, and are also known for their excellent machineability on automatic packaging equipment. The protective properties of PVDC coatings include: resistance to water, oil, grease, chemicals, including certain solvents, as well as very low permeability to water vapor, gases, and aromas(1,2,3). Although these properties of PVDC have made it very popular for packaging, PVDC presents the paper converter with the problem of blocking. Blocking is defined (4) as an undesired adhesion between touching layers of a material such as might occur under moderate pressure, temperature, or high relative humidity during storage or use. The objective of this study is to find possible ways to eliminate this blocking problem.

In addition to keeping PVDC coated paper from blocking the paper converter must also make it flexible. The reason for this is that in most applications of PVDC coated paper some degree of flexibility is required, especially in those applications where the coated substrate is to be subjected to either a scoring or a hard, sharp creasing action during the final utiliaztion (form and fill packages). PVDC coated paper exhibits its best barrier properties the greater its degree

of crystallinity. The greater its degree of crystallinity, however, the less flexible or more brittle the polymer becomes. Furthermore, requirements for flexibility and elasticity are in direct contradiction to those for optimum blocking resistance(5,6). At low levels of crystallinity (flexible coating) PVDC blocks front to back (adheres between concentric layers) in a rewound roll.

Several ways of approaching the problem of blocking have been found in the literature written on the subject of PVDC coatings(1,2,5-11). The use of a flexible first layer coating of PVDC with a more highly crystallized top coating of PVDC is one method of optimizing both the barrier properties and the resistance to blocking of PVDC coated paper(5,6). Another method is the addition of an anti-blocking agent to the PVDC coating or to the coating applied to the surface against which PVDC blocks(2,12). Also the degree of crystallinity can be controlled by the vinylidene content of the PVDC (crystallinity decreases with increasing amounts of comonomers) and by the rate and degree of drying of the PVDC coating(1,5-11). For the most part, however, this study will be concerned with the effects of anti-blocking agents.

HISTORICAL BACKGROUND AND DEVELOPMENT OF THE PROBLEM

Discovery of PVDC

The French chemist Regnault, in 1838, was the first to discover vinylidene chloride(1,13). Braumann, in 1872, and Ostromislenski later noted the influence of light on the precipitation of vinylidene chloride(7,13,14). In 1922 Brooks (13,15) indicated that halogenated ethylenes other than vinyl chloride and vinyl bromide showed a tendency toward polymerization. The first thorough examination of the apparent polymerization, however, was carried out by Feisst and Staudinger (1,13) in 1930 and the solid material was identified as polyvinylidene chloride (PVDC). This polymeric material was completely saturated and Feisst reported the polymer to be crystalline(13).

Development of PVDC and its Properties

The early vinylidene chloride polymers were not of a true film-forming variety. For this reason the addition of an external plasticizer was required in order to develop consolidated films with any degree of flexibility. This external plasticization consisted of either the chemical solvent type such as dibutylphthalate or the addition of a second, more flexible polymer resin(11). The addition of plasticizers, however, reduced the barrier properties of PVDC.

To overcome this problem of PVDC as well as its low thermal stability, systematic work on polymerization and copolymerization of vinylidene chloride was conducted in 1938

in the United States (mainly by Dow Chemical Co.) and in Germany (mainly by BASF) (1). Emulsion polymerization in an aqueous medium was found to be the most suitable method. Polymers obtained by this method using pure vinylidene chloride were found insoluble in the common solvents but would dissolve at about 100°C in such solvents as cyclohexanone and dimethylformamide. These pure polymers were highly crystalline and softened at about 200°C, decomposing at the same time.

It was found in these studies that only copolymers of vinylidene chloride had sufficient stability for processing. Copolymers with the following comonomers were examined thoroughly: acrylic esters, methacrylic ester, fumaric ester, maleic ester, vinyl acetate, vinyl ether, vinyl chloride, vinyl methyl ketone, and acrylonitrile(1). In order to maintain high barrier properties, however, a high percentage of vinylidene chloride needed to be present in the copolymer(1,2, 6,10,11).

In 1949-1951 BASF marketed plasticizer and solvent free aqueous PVDC copolymer emulsions containing a high percentage of vinylidene chloride (called Diofan). In order to obtain good film formation on the substrates, however, the film forming temperature of these products had to be as low as possible(1).

Another consideration was the influence of comonomers on the processing properties of the emulsion. One method of evaluating the influence of comonomers was the measurement

of the softening points of the copolymers., Methylacrylate as a comonomer was shown to give the lowest possible softening point in the desired range for high percentage vinylidene chloride copolymers(1). Therefore, most commercially available PVDC dispersions at that time contained methylacrylate as a comonomer and in some cases acrylonitrile(1).

The polymerization of vinylidene chloride is exothermic, occurs readily, and generally responds to the catalysts which are used with vinyl chloride(7). PVDC, however, differs from most vinyl polymers in showing well defined crystalline behaviour. Its physical properties are dependent primarily upon the state of molecular organization(1,7). Three states are distinguishable: amorphous, crystalline, and oriented. These states are not clear cut as they overlap to some extent. In common with most crystalline polymers, PVDC has a relatively sharp melting-point in the region of 160°C(7).

Barrier properties of PVDC are directly related to its degree of crystallinity. The higher the amount of crystallinity the better the barrier properties of the polymer. In the crystalline and oriented states PVDC is resistant to the action of most solvents, acids, and alkalis. It also has excellent aging properties and will not support combustion(7). Copolymerization to obtain process stability and flexibility, however, impairs or destroys the ability to crystallize depending on the nature and the amount of the comonomer. A reduction in the crystallinity of PVDC causes a reduction of its softening point and increases its solubility in organic

solvents. In general, copolymers which contain less than 70 per cent vinylidene chloride are non-crystalline(7).

Application of PVDC to Paper

In applying PVDC coatings to paper there are four main things to consider. These things are: the coating machinery, the base sheet, the drying of the PVDC film, and the addition of any additive to the PVDC emulsion. Any chemical addition to the PVDC emulsion will usually have an adverse affect on the barrier properties of the PVDC film.

Machines. There are several methods of applying PVDC to paper. These methods include: air-knife, metering bar, size press, rotogravure, and trailing blade(6,11,16,17). Literature on the subject indicates that the air-knife and metering bar coating methods are the most widely used.

The advantages and disadvantages of each machine that should be considered are: the uniformity (quality) of the PVDC film applied, the speed of application, the number of coating applications needed to get the desired coat weight, and the type of base sheet to be coated. Problems such as foam must also be considered because air can easily be incorporated into PVDC emulsions of high solids content causing a serious loss of barrier properties. Both the air-knife and the metering bar coating methods are capable of applying good continuous films of PVDC, exhibiting high barrier properties, over a wide range of coat weights.

Base Sheet. Necessary for good PVDC film formation is a base sheet which is smooth and has the ability to hold the water

emulsion on the surface. Machine calendered or mechanically polished sheets give the desired smoothness. The utilization of a clay-coated surface as a precoat treatment for PVDC resins is the most generally satisfactory way of obtaining smoothness and the desired water holdout. The precoat, however, should be applied under conditions which do not favor the drainage of the adhesive from the uppermost surface.

It has been found that the absence of an adequate amount of adhesive in the surface layer of the precoat gives rise to an "instantaneous dewatering" of the emulsion as it is brought into contact with the coated surface. This instantaneous dewatering will cause the individual particles of the emulsion to coalesce into specks, and these specks will give rise to pinholes in the case of air-knife applied coatings, or scratches in the case of metering bar applied coatings(11).

Adhesive (binder) migration has been studied by many individuals(18-29). These studies have indicated that high solids coatings are less prone towards binder migration than low solids coatings. Also migration in the direction of the border between coating and base stock is governed mainly by the absorbency of the paper base; migration towards the surface of the coating is determined by the drying rate and increases with increasing rate of evaporation. The type of adhesive used (30,31) and the degree of particle packing (32) affect the rate of drying and therefore the amount of binder migration. One way of evaluating coating adhesion is by making wetting angle determinations(19).

Drying Methods. Aqueous PVDC dispersions contain the polymeric material in the form of uniformly distributed very small particles(8). During drying of the dispersion, these small spherical particles must coalesce and form a compact, coherent layer. Only then will optimum protective properties of the coated paper be achieved.

The initial objective should be to raise the solids level as rapidly as possible (by evaporation) so that the coating loses its fluidity(10). If initial dewatering is delayed, it will occur by absorption into the porous web. This can have the effect of producing a powdery polymer deposit which will adversely affect the barrier properties of the coating. Infrared radiant dryers, employed ahead of a hot air dryer, can help effect this initial drying step. The first phase is known as "thermal fixation"(8).

Phase two may be considered that portion of the drying process in which solids concentration is increased from 70 per cent to about 86 per cent at which level film formation takes place(10). This phase can be achieved using a drying tunnel.

After agglomeration to a closely packed layer, the polymer particles can no longer move freely, and only the space between the polymer spheres is occupied by water(8). The colloidal interaction between emulsifier, particle surface, and liquid phase, and the water absorption of the substrate have a certain influence on the coalescence of the particles(8). According to G. L. Brown (8), the capillary pressure is the

decisive factor responsible for film formation. This factor (P) can be determined approximately according to the following equation: $P = 2\sigma/R$

Where σ = surface tension
R = radius of the particles

Therefore, temperature, flow resistance, and hence drying speed and mass of the particles are all important.

The second phase is followed by a thermal aftertreatment, which is also referred to as the "fusing zone", in order to impart optimum properties to the coating(5,8). This is often done with IR radiators. This writer, however, feels that the term "fusing" is incorrect. What actually happens during thermal aftertreatment is a further crystallization of the PVDC film. This crystallization is achieved by the elimination of trace quantities of water from the dried PVDC film.

One precaution, however, must be observed in the drying of PVDC coated paper. This precaution is not overdrying the paper. Overdrying will cause the paper to be brittle and may tend to cause the PVDC coating to discolor or blister(8,11).

The more common crystalline copolymers show their maximum rates of crystallization in the range of 80-120°C(2). PVDC itself probably crystallizes at a maximum rate at 140-150°C, but the process is difficult to follow because of severe polymer degradation(2). The copolymers may remain amorphous for a considerable period of time if quenched to room temperature. The induction time before the onset of crystallization depends on both the type and amount of comonomer; PVDC itself crystallizes within minutes at 25°C(2). A more detailed dis-

cussion of the drying of PVDC films and the crystallization of PVDC can be found in publications by BASF and others(1,2,5,7, 8,10).

Chemical Additions to PVDC. The addition of any chemical to the PVDC emulsion tends to lower the barrier properties of the PVDC film. Therefore, any additive used to improve either the flexibility or the blocking resistance of a PVDC coating should be used with caution. Also because PVDC coated paper is used in food packaging all FDA regulations must be met by the additives.

Discussion of Blocking

Causes. Blocking can be caused by several factors. Some of these which the paper converter must contend with are: pressure, temperature, relative humidity, nature and ratio of binder to pigment, binder migration (18-29), and the degree of crystallinity of PVDC films(9,33). The effect of pressure and temperature on the adhesion of two surfaces both containing polymers is discussed in the book "Autohesion and Adhesion of High Polymers"(34).

This type of surface is present when a paper web is coated with PVDC (polymer) on one side and a clay-coating (containing polymeric adhesives) on the other side. The book describes this type of adhesion as self-diffusion (autohesion). For a given polymer system, factors which influence autohesion are: duration of contact, pressure, temperature, and thickness of the polymer layers(34). According to the author of this book autohesion increases with contact time, and pressure serves to bring the blocking surfaces into close contact. He goes

on to say that temperature influences the thermal motion of the links of chain molecules thus causing interweaving of high polymer chains. Voyutskii (34) also says, "Molecules with long branchings probably cause increased autohesion because such molecules are firmly anchored in the layer of material into which they diffused, and also because they have many end segments capable of diffusion." Autohesion appears to be related to binder migration and the degree of crystallinity of PVDC.

It is known that the more crystalline the PVDC film the more resistant it is to blocking. If the film is made more highly crystalline the effect of pressure and contact time, which are important to autohesion, will have less influence on the contact of the two surfaces. Therefore, one of the mechanisms of blocking appears to involve autohesion.

Another cause of blocking that has been mentioned is that of too much moisture on an opposing clay-coated surface. Too much moisture within the PVDC film inhibits crystallization and thus decreases blocking resistance. An excess of moisture on the clay-coated surface could give the molecules of the two closely packed surfaces a vehicle by which to move, thus producing an effect similar to that of the interweaving of polymer chains occurring in autohesion. A detailed analysis of the "adsorption theory of adhesion", which attributes adhesion to van der Waals interaction, and "diffusion theory of adhesion" can be found in Voyutskii's book(34).

Although the manufacturers of PVDC emulsions are concerned with the blocking problem none has introduced to date any new ideas or mechanisms explaining the problem. The most established and published answer to the problem of blocking centers on the crystallizaion of PVDC (1,2,5-11), which is influenced by its comonomers and degree and rate of drying.

Ways of Eliminating Blocking. As already mentioned, increasing the degree of crystallinity of the PVDC film increases blocking resistance. This, however, causes a decrease in the flexibility of the coated paper which the paper converter must be concerned with. Ways of increasing the degree of crystallinity are: by using a PVDC emulsion containing a high vinylidene chloride content (10), by completely drying the PVDC film (11,33), and by the choice of comonomers used(1).

The barrier properties and blocking resistance of PVDC, which are dependent upon the degree of crystallinity, are brought about by the close-packing of the chlorine atoms in the polymer(10). This imposes two prerequisites on the polymer: vinylidene chloride content should be maximum; comonomers should be compact molecules(10). Close packing of the chlorine atoms in PVDC, offsetting the effects of autohesion, are responsible for the crystallinity of the polymer.

Also by increasing the degree or the rate of drying of the PVDC film, crystallinity can be increased. Complete drying of the PVDC film before the paper web is wound up will eliminate blocking. The paper converter, however, must be careful not to over-dry the coated paper thus causing a loss

in flexibility and also a possible introduction of steam blisters which seriously affect barrier properties. If the rate of drying is too slow initial dewatering will occur by absorption into the paper web and thus cause a loss in barrier properties(8,10). If the rate of evaporation is too fast the adhesion of the PVDC film to the paper surface will be affected and the formation of steam blisters is likely(8). Generally, it can be said that, in order to get optimum barrier properties and blocking resistance, there is a delicate balance between underdrying and overdrying as well as the rate of drying of the PVDC film.

An obvious question at this point is, what amount of moisture may be present in dried PVDC coated paper and still constitute complete drying of the PVDC film? And further, does the temperature of the dried PVDC coated paper influence the amount of moisture that can be present without causing blocking? According to Voyutskii (34) temperature plays an important part in autohesion (one mechanism by which blocking apparently occurs). These questions are not completely answered in the literature published on the subject. It is generally agreed that a rewound roll with a high temperature or with a high amount of moisture in the PVDC film will tend to block. The actual interaction between temperature and moisture of PVDC coated paper, however, apparently has not been studied. For a complete understanding of the problem of blocking of PVDC coated paper a thorough study of drying rate and drying history, along with a study of the interaction between temperature and moisture should be undertaken.

Another way of preventing blocking is by eliminating any excess moisture on the clay-coated surface and by carefully controlling the binder migration in the coating. By eliminating excess moisture there is less chance of any polymer molecules interweaving and causing blocking. The effect of binder migration (18-29), in conjunction with excess moisture, influences the availability of binders having an affinity for PVDC to form an autohesive or any other kind of bond. Migration of binders to the surface may cause separation within the pigment coat or blocking if soft, thermoplastic, or hydrophilic types are used(9). Generally, binders with less plasticity and low moisture absorption are preferred(33).

A third way of preventing blocking is the use of anti-blocking agents in the PVDC emulsion or in the clay coating. The addition of anti-blocking agents to the PVDC emulsion, however, adversely affects barrier properties and are therefore not adviseable to use. Only small additions of some silicones and wax emulsions are compatible with PVDC emulsions.

Such anti-blocking agents as silicones, wax emulsions, sodium alginates, and silicates can be used in the clay coating without adversely affecting the barrier properties of the PVDC film. The effectiveness of these additives and their effect on printing quality of the clay-coated surface, however, are the objects of this study. Silicones because of their heat resistance, high order of stability, and water resistance function as release agents in either PVDC emulsions or clay-coatings(7,35,36). Dispersing agents, otherwise known

as surfactants, also function as release agents(10). Wax emulsions serve as lubricants and affect the flow characteristics of the coating (binder migration) (29) as well as increase the coating smoothness. Wax emulsions are also claimed to give better resistance to water penetration(37). The general properties of silicones (38) and wax emulsions (37) indicate that if they are used in the proper amount and are compatible with the coating they should be good anti-blocking agents.

One last way that has been mentioned to prevent blocking of PVDC coated paper is that of using chill rolls following drying(9-11). Since PVDC coatings are thermoplastic materials, they may block when rewound at high temperatures. It has been claimed, however, that blocking is minimized if the web is brought back to room temperature(10). This is only partly true according to Patton(10). Patton says, "While temperatures in the roll above 140°F are hazardous from the point of view of blocking, in the absence of a back-side coating, and with normal drying, blocking has not been a problem up to 140°F." This type of blocking is directly related to autohesion which is affected by high temperatures.

The elimination of blocking can be approached from any of the above mentioned methods. The best method, however, for one mill may not be the best for another mill. Economics, available equipment, base sheet qualities, etc. should all be evaluated to determine which method or combination of methods will eliminate the problem at the lowest possible cost.

PRESENTATION OF PROBLEM

The increased demand for flexible PVDC coated paper has forced the paper converter to go to higher speeds of production. This increase in speed has accentuated the paper converter's problem of PVDC blocking front to back with a clay-coated surface. As already discussed several approaches to the problem can be taken. Generally, the problem is due to incomplete crystallization of the PVDC film when the paper is rewound.

Obviously, the paper converter can increase the degree or rate of drying to effect a higher amount of crystallization of the polymer. The paper converter, however, must be careful not to lose the desired flexibility of the paper due to the increase in crystallization. Also a change in the type and ratio of comonomer can improve crystallization. This, however, may not be desirable for other reasons. Economics of solving the problem must also be looked at. For these reasons a logical approach to the problem of blocking may be the use of anti-blocking agents.

The use of any anti-blocking agent must meet FDA regulations because PVDC coated paper is used in food packaging. Also the effect that the additive has on the printing quality of the clay-coating must be checked. Other problems that might be anticipated using these additives are: pH, viscosity, and stability under high shear.

This investigation will focus on the addition of vary-

ing amounts of different wax emulsions and silicones to different coating formulations. The objective being to eliminate blocking without adversely affecting the coating quality. The elimination of blocking without affecting sheet flexibility, barrier properties, or printing properties using an anti-blocking agent is the object of this study.

EXPERIMENTAL

Introduction

This experiment was designed to evaluate the blocking resistance of several anti-blocking agents in different coating formulations. Initially the coatings were checked for pH and viscosity to determine what effects the anti-blocking agents had in each coating formulation. The coatings were then applied using an automatic trailing blade bench coater and each coated sheet of paper was dried on a hot plate. After drying, each coated sheet was examined for blocking resistance and printing qualities.

Two different base sheets were used in the experiment. One having a very low size and the other a much higher size. The use of two differently-sized base sheets should give some indication of the binder migration. The furnish of these two base sheets is shown in Table I.

Table I. Base Sheet Furnish

A	B
20% Hardwood	40% Hardwood
80% Softwood	60% Softwood
67 parts broke	35 parts broke
Size (Ink Float)-2 sec.	Size (Ink Float)-40 sec.
Basis weight - 20½ lb.	Basis weight - 30 lb.

Coating Make-up

The order of addition for each coating formulation was the same, with each coating being made up using a Cowles dissolver. First the solids concentration was determined, then

the desired amount of water was placed in a large stainless steel beaker. Pigment dispersants were then added in this order: sodium tetraphosphate, bridged sodium hexametaphosphate, and then the sodium salt of a complex carboxylic acid. After these dispersants had mixed for a short period of time the pigments were added, rutile titanium dioxide first followed by calcium carbonate, and then No. 2 clay. Each pigment was allowed to mix for 5 minutes before the addition of the next pigment or coating ingredient. Protein followed by starch were then added to the coating. At this point a small amount of ammonia was added for pH control. Now the synthetic adhesives were added followed by the anti-blocking agents. The coating was then allowed to mix for 15 minutes.

The coating formulations are shown in Table II and Table III. The properties of the anti-blocking agents used are shown in Appendix I.

Evaluation of the Liquid Coatings

Viscosity. The Brookfield RVF-100 model Synchro-lectric viscometer was used to measure the flow properties of the coatings. This instrument gave a quick indication of whether the coating was thickened or thinned by the anti-blocking agent.

pH. pH was checked using the Fischer Accumet pH meter model #210. This test was run to be sure that the coating pH was near 9.5. This made possible the determination of any anti-blocking agent adversely affecting the coating.

Solids. This was determined to serve as a check on the ac-

Table II. First Laye. Coating Formulations
Dry Weight in Grams

	A	B	C	D	E	F	G	H	I	J	K	L
Sodium Tetraphosphate	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975
Bridged sodium hexametaphosphate	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sodium salt of complex carboxylic acid	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Rutile Titanium Dioxide	300	300	300	300	300	300	300	300	300	300	300	300
Calcium Carbonate (precipitated)	250	250	250	250	250	250	250	250	250	250	250	250
No. 2 Clay	650	650	650	650	650	650	650	650	650	650	650	650
Protein (soybean) - low viscosity	12	12	96	96	96	96	12	12	12	12	12	12
Starch (oxidized corn) - Clinton XS	48	48	---	---	---	---	48	48	48	48	48	48
Styrene-Butadiene Latex (Dow SD-594)	180	180	144	---	---	144	180	180	180	---	---	---
Acrylic emulsion (Rhoplex B-15)	---	---	---	180	120	---	---	---	---	---	---	---
Polyvinyl Acetate (National 25-1104)	---	---	---	---	---	---	---	---	---	180	180	180
Nopco wax emulsion (DS 101)	---	144	72	---	144	---	---	---	---	---	---	144
Nopco wax emulsion (Koy)	---	---	---	---	---	120	---	---	---	---	---	---
Hercules wax emulsion (Paracol 404 G)	---	---	---	---	---	---	---	---	---	---	---	---
Dow wax emulsion (Product X)	---	---	---	---	---	---	---	24	48	---	96	---
Silicones	---	---	---	---	---	---	---	---	---	---	---	---
Viscosity, cp, Brookfield 100 rpm 90°F	851	870	560	345	392	860	710	---	---	383	---	---
pH	9.7	9.7	9.5	9.6	9.8	9.7	9.8	---	---	9.7	---	---
Solids (theoretical), %	60.0	58.0	56.0	56.0	56.0	56.0	58.0	---	---	58.0	57.5	56.0
Solids (actual), %	61.3	57.1	---	---	---	---	57.7	---	---	58.0	---	---

Table II. First Laye. oating Formulations
Dry Weight in Grams (continued)

	M	N	P	R	S	T	V	W	X	Y	Z	AA	BB
Sodium Tetraphosphate	0.975	2.0	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975	0.975
Bridged sodium hexametaphosphate	2.0	---	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sodium salt of complex carboxylic acid	0.3	---	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Rutile Titanium Dioxide	300	---	300	300	300	300	300	300	300	300	300	300	300
Calcium Carbonate (precipitated)	250	---	250	250	250	250	250	250	250	250	250	250	250
No. 2 Clay	650	1200	650	650	650	650	650	650	650	650	650	650	650
Protein (soybean) - low viscosity	12	24	24	24	24	12	12	12	12	12	12	12	12
Starch (oxidized corn) - Clinton XS	48	96	120	168	120	144	48	48	48	48	144	96	48
Styrene-Butadiene Latex (Dow SD-594)	---	120	96	96	96	96	180	180	180	180	180	180	180
Acrylic emulsion (Rhoplex B-15)	---	---	---	---	---	---	---	---	---	---	---	---	---
Polyvinyl Acetate (National 25-1104)	180	---	---	---	---	---	---	---	---	---	---	---	---
Nopco wax emulsion (DS 101)	---	---	---	---	144	---	---	---	---	---	---	---	---
Nopco wax emulsion (Koy)	---	---	---	---	---	---	---	---	---	---	---	---	---
Hercules wax emulsion (Paracol 404 G)	96	---	---	---	---	---	---	---	---	---	---	---	---
Dow wax emulsion (Product X)	---	---	24	---	---	48	---	---	---	96	96	96	---
Silicones	---	---	---	---	---	---	DC-24 100ppm	FG-10 100ppm	Anti-foam C33ppm	---	---	---	---
Viscosity, cp, Brookfield 100 rpm 90°F	---	---	---	---	---	---	---	---	---	---	666	658	1024
pH	---	---	---	---	---	---	---	---	---	---	9.7	9.6	9.5
Solids (theoretical), %	57.5	60.0	54.0	54.0	54.0	54.0	58.0	58.0	58.0	54.0	54.0	56.0	60.0
Solids (actual), %	---	---	---	---	---	---	---	---	---	---	---	55.6	59.0

Table III. Top Layer Coating Formulations
Dry Weight in Grams

	1	2	3	4	5
Sodium Tetraphosphate	1.8	2.0	2.0	2.0	1.8
No. 2 Clay	1200	1200	1200	1200	1200
Protein (soybean) - low viscosity	12	144	144	144	12
Starch (oxidized corn) - Clinton XS	72	---	---	---	96
Styrene-Butadiene Latex (Dow SD-594)	180	96	---	---	180
Acrylic emulsion (Rhoplex B-15)	---	---	96	96	---
Nopco wax emulsion (DS 101)	---	144	144	---	---
Dow wax emulsion (Product X)	96	---	---	96	96
Viscosity, cp, Brookfield 100 rpm 90°F	---	1480	656	2620	506
pH	---	9.3	9.3	9.4	9.3
Solids (theoretical), %	54.0	56.0	53.0	56.0	54.0
Solids (actual), %	---	55.2	52.7	55.5	54.1

curacy of the theoretical make-up and as a rough check against the other coatings when comparing viscosities.

Several viscosity measurements, pH readings, and per cent solids determinations were not taken due to the fact that each of these coatings were made-up using 100 gram aliquots of a pigment slurry. It was intended that any of these coatings exhibiting reasonable blocking resistance would be made-up in larger amounts and more thoroughly evaluated.

Method of Application and Drying of the Clay-Coatings

The clay-coatings were applied using an automatic laboratory trailing blade bench coater. The target coat weight to be applied with the first layer of coating was 4.0 lb./ream (ream = 3300 sq-ft). Due to inherent operating conditions it was not always possible to apply exactly 4.0 lb./ream. Therefore, any coat weight which was plus or minus 0.2-0.3 lb./ream from 4.0 lb./ream was accepted. The top layer of coating had a target coat weight of 2.0 lb./ream. A laboratory check on blocking and Diamond National test results obtained after drying two different samples of the same coated sheet differently (one on a hot plate and the other in an oven) showed no difference. Therefore, all coated sheets were dried on a hot plate.

Method of Application and Drying of the PVDC emulsion

The PVDC applied was an experimental latex (XD-7385.01) made by the Dow Chemical Company(39). It is a terpolymer containing a 90-plus percentage of vinlyidene chloride. This

latex possesses very low foam characteristics and can be applied by any of the conventional coating techniques currently used to coat saran latexes (PVDC) on a variety of substrates. This latex can be dried by infrared, convection air, or dielectric techiques according to Dow. When convection air drying is used, Dow claims that, a short, intense drying cycle is usually more efficient than a longer, low temperature schedule. Dow suggests a drying temperature range of 300-350°F. The optimum barrier properties of the experimental latex are obtained when it is dried at an elevated temperature.

Application of the PVDC emulsion was done using a drawdown rod. The film was air-dried for about 5 minutes. This type of application and drying served the purpose of accentuating the blocking tendency of PVDC because it gave a freshly coated PVDC film which was incompletely crystallized. Various amounts of coat weight were applied in order to contrast the blocking tendency of low coat weights with high coat weights. The PVDC emulsion was always applied to base sheet B (see Table I) having a clay precoat. Blocking of a freshly coated and incompletely crystallized PVDC film against a clay-coated surface maximized the tendency of PVDC to block. Using this approach the effect of each anti-blocking agent was evaluated for its resistance to blocking.

Evaluation of Coated Paper

Sheffield Smoothness. This test was designed to measure the smoothness of a sheet of paper by means of the rate of air

leakage between the paper surface and a standard smooth surface. A comparison of the coated surfaces having different coating formulations was obtained using this test.

Diamond National Print Smoothness Tester. This is one way of evaluating a coated paper surface for printing quality based on the smoothness of the coated surface. This tester is essentially a bench model gravure press. When used in conjunction with a standardized cylinder, the tester provides a numerical rating of sample printability. This rating is the measurement of the number of unprinted or missing ink dots (skips) on the coated surface. The lower the number of ink dot skips the better the printing quality of the coated surface.

IGT Pick Test for Paper Surface Strength. This test is a Tappi suggested method (T 499 su-64). The IGT printability tester is essentially a miniature cylinder printing press which operates at accelerating velocity. The picking force on the surface of the paper under test depends on the viscosity of the ink or oil used and the velocity at which the separation of the ink film and paper occurs. With a given ink viscosity, a numerical rating can be based on the distance along the strip at which surface failure occurs, since the rotating printing sector is attached to a pendulum arm which falls with accelerated motion due to gravity. This test was run using a #6 tack ink with both the pendulum drive and the spring drive.

K&N Ink Absorbency Test. The rate of absorption of an es-

pecially formulated oil-base ink by paper surfaces results in corresponding losses in brightness. The ratio of the brightness of the paper where the ink has entered to the original brightness is the value to be determined. This test was used to determine the effect each anti-blocking agent had on ink absorbency.

Consolidated Pick-Rub Test(40). This test was used to visually evaluate the wet pick and rub resistance of a coated paper surface. The adhesive bond of coating to the base sheet and the cohesive strength of the coating itself are both tested with this instrument. The instrument is designed to simulate offset press conditions of moisture, pressure, and rub. Severity of the test can be increased by introducing and increasing the rub factor. This test relates to both image and non-image area piling for sheet fed and web offset printing processes.

Test samples were rated by visual comparison in a range from 0 to 4. Samples showing considerable pick were rated 0 and samples showing no pick were rated 4.

Consolidated Blocking Test[1]. This test is more severe than Tappi Standard T 477 m-47. The test equipment consists of several rectangular bars weighing 12 pounds each, one solid steel cylinder approximately one square inch in area, one large solid circular disk, and a stop watch.

Place the paper surfaces to be blocked, front to back, on the large solid circular disk with the solid steel cylinder

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[1]To the best of this writer's knowledge this test was developed by Consolidated Paper Company.

on top of them. Next place as many of the rectangular bars (by centering) on top of the solid steel cylinder as are necessary to achieve the desired blocking pressure. Then start the stop watch. After 5 minutes have elasped remove the rectangular bars and separate the two paper surfaces.

Examine the surfaces for both coating and fiber picking. Record the results as: no picking; slight picking; moderate picking; and heavy picking. If no picking occurs the two paper surfaces are considered as not blocking.

This blocking test exhibits some of the factors which are important in autohesion such as pressure and contact time.

During this experiment several different blocking pressures were used. It was apparent, however, that any pressure under 60 lbs. would be very inadequate for simulating actual roll conditions. Therefore, most of the blocking tests were run with 60 or more pounds of pressure. The more pressure that could be applied without causing blocking the better the anti-blocking agent was. Trying to compare a slight pick at 60 lbs. to a heavy pick at 96 lbs., however, is impossible. The only thing that can be said is that a slight pick at 60 lbs. will probably be a heavy pick at 96 lbs. This type of comparison is worthless, however, because any evidence of picking means that a blocking problem still exists.

PRESENTATION AND DISCUSSION OF RESULTS

Results of the laboratory investigation of anti-blocking agents are tabulated in Table IV and Table V.

Coating Evaluation

Anti-blocking agents showed little if any adverse affect on the pH of the coatings. The viscosity measurement, however, indicated that all of the wax emulsions increased viscosity to some degree. This indicates colloidal stability of the coating may have decreased. The synthetic wax emulsion DS-101 (M.P. 215°F) only adversely affected viscosity when starch was in the coating formulation. This indicates that DS-101 should only be used in those formulations without starch if viscosity is going to be a problem. The wax emulsion Koy (M.P. 185°F) increased viscosity significantly even without starch being present. Although Product X increased viscosity, it appeared to affect the flow characteristics of the coating less than the synthetic wax emulsion DS-101 (M.P. 215°F). Under high shear, however, the coating formulation "AA" containing Product X was shear thinning.

One way of eliminating the increase in viscosity caused by the addition of wax emulsions to the coating is by lowering the solids content of the coating. This, however, could lead to problems in getting the desired coat weight.

Coated Paper Evaluation

The surface strength of the first layer of coating as evaluated by the IGT test showed Product X to be far super-

Table IV. Surface Evaluation of the Coated Paper

Coating	Sheffield Smoothness (cm^3/min)	Diamond National (ink skips)	% K&N	IGT (cm/sec)[1]		Pick-Rub Test	
				Pendulum Driven	Spring Driven	Straight	1/2 Turn
A	---	---	60.3	68cf	50cf 143s	4	2
B	---	---	62.1	30cf 107s	0cf 123s	4	3
C	---	---	66.6	---	---	4	3
D	---	---	66.4	---	---	4	3
E	---	---	61.0	---	---	4	3
F	---	---	68.5	---	50c 95f 274s	4	3
G	41.0	---	59.9	---	---	4	2
H	51.2	---	67.0	---	---	4	2
I	44.8	---	69.3	---	---	4	3
J	61.8	20	57.9	---	---	4	2
K	68.6	41	65.3	---	---	4	3
L	72.4	27	62.1	---	---	-	3
M	70.0	---	63.0	55cf	0cf 117s	4	3
N	71.0	---	51.8	---	---	4	2
P	60.6	44	64.6	---	---	3	0
R	61.0	27	64.1	---	---	3	0
S	63.6	24	68.6	---	---	3	2
T	54.4	34	72.0	---	---	3	1
V	---	---	61.4	---	---	4	1
W	44.0	12+	63.9	---	---	4	1
X	---	---	67.3	62cf	33cf 274s	4	2
Y	43.5	15	74.8	---	---	4	3
Z	30.8	10+	85.3	115 clear	158c	3	2
AA	29.5	14+	73.8	---	---	4	1
BB	24.0	8+	68.5	---	---	4	2
1	16.0	14	85.6	115 clear	95c	3	1
2	13.0	9	81.4	115 clear	147cf	4	3
3	16.0	18	82.9	113c	104cf	4	3
4	12.0	2	83.3	115 clear	77c	4	3
5a	15.3	10+	85.0	113c	---	3	1
5b	8.2	2	77.6	112c	217cf	3	2

[1] c = coating
f = fiber
cf = coating-fiber
s = split

Table V. Blocking Test Results

Coating	Base Sheet	Coat Weight (lbs/ream)	PVDC Weight (lbs/ream)	Blocking Results (lbs of pressure)
A	A	3.9	5.9	Picked at 12
B	A	3.8	5.9	Picked at 12
C	A	3.7	6.0	Slight pick at 12
D	A	4.0	6.0	Slight pick at 12
E	A	3.7	6.0	Picked at 12
F	A	4.0	6.0	Slight pick at 12
G	A	3.9	4.1	Picked at 12
H	A	3.9	3.9	Picked at 12
I	A	3.7	3.3	Slight pick at 12
J	A	4.0	6.0	Picked at 60
K	A	3.6	6.0	Slight pick at 60
L	A	3.7	6.0	Picked at 60
M	A	4.1	5.6	Picked at 60
N	A	4.0	4.2	Picked at 60
P	A	3.9	4.0	Slight pick at 60
R	A	4.1	4.0	Slight pick at 60
S	A	4.0	4.0	Picked at 60
T	A	3.9	4.0	Very slight pick at 60
V	A	3.9	3.8	Picked at 60
W	A	4.3	3.8	Picked at 60
X	A	4.2	3.8	Picked at 60
Y	A	4.1	3.9	Slight pick at 96
Y	A	4.1	10.1	Picked at 96
Z	B	3.9	5.4	No pick at 96
AA	B	4.0	10.1	No pick at 96
BB	B	4.0	11.3	Picked at 96
1	Z	2.0	5.3	No pick at 96
2	AA	2.0	9.0	Picked at 96
3	AA	2.1	9.0	Picked at 96
4	AA	2.1	9.0	Heavy pick at 96
5a	AA	2.0	7.0	No pick at 96
5a	AA	2.0	13.0	Slight pick at 96
5b	BB	2.1	7.0	No pick at 96
5b	BB	2.1	13.0	Slight pick at 96

ior to the other anti-blocking agents. A comparison of coatings "A" and "B" showed that DS-101 weakened the surface strength of the coating. Coating "F" containing Koy wax emulsion with no starch and an increased amount of protein compared to coating "A" showed slightly better surface strength. Paracol 404G used in coating "M" gave results similar to coating "B" having DS-101. The silicone antifoam C gave similar results to the Koy wax emulsion. Coating "Z" containing 12 parts starch and 8 parts Product X gave results showing a much higher surface strength than all of the other first layer coatings. Comparing coatings "A" and "Z" indicates that either Product X or the additional starch, or maybe the combination of the two greatly enhanced the surface strength of the coated paper. It is more than likely, however, that the additional starch was responsible for the improved surface strength because of the increase in the binder to pigment ratio. Product X, however, did not weaken the coated surface as did DS-101. Coating "Z" gave the best IGT test results.

The coatings with Product X also gave good results with the Pick-Rub test when not mixed with a large amount of starch. Silicones, on the other hand, gave poor Pick-Rub test results. In general, however, all the wax emulsions improved the coated surface, according to the Pick-Rub test, when not formulated with large amounts of starch. The reason for the coatings containing high starch content giving poor Pick-Rub test results was probably due to the fact that starch has very poor water resistance (a drop of water was used in the test).

The K&N ink test results showed that the coatings with Product X (K,T,Y,Z,AA) gave high values of K&N ink holdout. Coatings containing the synthetic wax emulsion DS-101 (M.P. 215°F), the wax emulsion Koy (M.P. 185°F), and the fully refined paraffin Paracol 404G (M.P. 156°F) showed moderate to high K&N ink holdout. The silicones also showed moderate values of K&N ink holdout. Starch again, however, was influential on the test results. No starch in the coating or high amounts of starch in the coating gave high K&N ink values. Moderate amounts of starch in the coating, however, gave lower K&N ink values. Depending on the desired printing quality high K&N ink holdout may be good. Too much holdout, however, can cause printing problems. None of the coated paper showed any signs of mottle and therefore the anti-blocking agents did not affect the uniformity of the coated surface.

The top layer of coating showed similar results to those of the first layer of coating. The top coating, however, was influenced by the first layer of coating as shown by the K&N ink values for coated samples 5a and 5b (5a and 5b differ in the first layer of coating only). Coated samples 5a and 5b also showed a difference in Diamond National test results. If the first layer of coating had poor quality the top coating generally also gave poor quality. It is hard if not impossible to cover up a weakness in the first layer of coating with a light top coating.

The blocking resistance desired was only achieved by using a high starch content and a high Product X content (coatings

Z,AA,1,5a,5b). These coatings would not block under a pressure of 96 lbs. The Diamond National test, however, showed a high number of skips if both the first layer of coating and the top layer of coating were made anti-blocking towards PVDC. If, however, just the top coating was made anti-blocking toward PVDC then a very low number of skips was obtained.

Comparison of coatings "G" and "H" showed that Product X improved Sheffield Smoothness and increased K&N ink holdout. Table V shows the results that the same coated sample had when blocked against two different PVDC coat weights. Coatings "Y", "5a", and "5b" showed that the heavier the PVDC coat weight the more picking (blocking) that took place. This indicates that the PVDC film was less crystalline and thus the polymer molecules necessary for interweaving (autohesion) were more available.

Product X for an unknown reason has the ability to prevent autohesion from taking place. Starch by itself can also prevent blocking. The large amounts of starch needed, however, interfered with printing qualities. The film forming properties of starch were probably the main reason for it being blocking resistant. For whatever reason, Product X does not appear to weaken surface strength; it appears to improve printability and, most important, it prevents blocking. Probably its mechanism or means of preventing blocking has something to due with the way it modifies flow properites (binder migration) of the coatings. If autohesion is the main cause of blocking then the ability of Product X to eliminate blocking must have something to due with its affect on polymeric binder migration, and also on its film forming properties.

CONCLUSIONS

The objective of this study was to find an anti-blocking agent that could be added to a clay-coating without adversely affecting the printability of the clay-coated sheet, and still prevent the PVDC film from blocking front to back. Based on the information gained during the laboratory investigation of anti-blocking agents there was only one additive that filled these needs. That additive was Product X, an experimental paraffin wax emulsion. Product X, however, only worked effectively when used in large amounts and with large amounts of starch.

Further work needs to be done to determine exactly what the chemical or physical interaction between Product X and starch was that made the coating blocking resistant. Also the flow properties of the clay-coating containing Product X should be examined to determine the effects of Product X on binder migration. Also clay-coatings containing Product X should be made up at a higher solids content to compensate for the shear thinning effect that Product X has, under high shear, in a clay-coating.

The results of this study indicate that an actual production machine trial should be run to determine whether or not the blocking resistant coating (AA,5a,5b - containing Product X) in conjunction with thorough drying (crystallization) of the PVDC film will prevent front to back blocking in a rewound roll.

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APPENDIX I

Properties of Anti-blocking Agents

1. A fully refined paraffin wax (Hercules) - Paracol 404G

Total Solids, % by weight	47
Wax melting point, °F	156
Wax Color	White
Emulsion pH	6.0-6.5
Density, pounds per gallon	8.0
Average particle size, microns	1-2
Mechanical Stability	Good
Chemical Stability	
Acids	Stable
Alkalies	Stable
Alum (other bi- and tri-valent inorg. salts)	Stable
Effect of freezing	Adverse

2. A synthetic wax emulsion (Nopco) - Nopcosize DS-101

Color	White
Solids	40 ± 1%
pH	8.5-9.5
Particle size (micron)	0.1-0.5
ASTM M.P. (°F)	215
Oil Content MIBK	1%
ASTM Penetration @77°F	1.5
Compatibility	Compatible with most anionic and nonionic papermaking chemicals; such as starch, PVA, latices.
Stability	Unstable below pH of 7.

3. A wax emulsion (Nopco) - Nopcosize Koy

Appearance	Fluid, white emulsion
Solids	30%
pH (2% solution)	7.0
Melting Point of wax	185°F
Pounds per gallon	8.0

4. A fully refined paraffin wax emulsion (Dow) - called Product X Experimental product.

Total solids, % by weight	50
Melting Point, °F	151-153
Color	White
Oil Content %	0.2
pH	6.0-7.0
Average particle size - micron	1
Pounds per gallon	8.1
Mechanical Stability	Good
Chemical Stability	Stable to acid, alkalis, most electrolytes

5. Silicone emulsion (35% dimethyl polysiloxane fluid) (Dow Corning) - Dow Corning 24

Percent silicone fluid	35
Color	White
Consistency	Water thin
Specific Gravity @77°F	0.997
Type of emulsifier	Essentially nonionic
pH	8.0
Suitable thinner	Water
FDA status	100 ppm (maximum)

6. Silicone emulsion (Dow Corning) - Antifoam FG-10

Percent active defoamer	10%
Consistency	Light pourable cream
Specific Gravity @77°F	1.0
Color	White
pH	3-5
Type of emulsifier	Nonionic
Suitable diluent	Water
FDA status	100 ppm (maximum)

7. Silicone emulsion (Dow Corning) - Antifoam C

Percent active defoamer	30%
Consistency	Pourable cream
Specific Gravity @77°F	1.0
Color	White
pH	4
Type of emulsifier	Nonionic
Suitable diluent	Cool water
FDA status	33 ppm (maximum)